

PATENT CLAIMS

1. A method for recycling metal pickling baths, including the associated rinsing baths and air washers, having the following steps:
 - a) converting the free acids present in the liquid waste streams to be treated into the metal salt form before recycling,
 - b) separating water from the largely acid-free metal salt solution obtained in order to obtain a concentrated metal salt solution, and
 - c) supplying the concentrated metal salt solution to a thermal method to obtain metal oxides and free acids.
2. The method according to Claim 1, characterized in that the acid waste streams from the pickling baths and the rinsing baths/air washers are each subjected to a separate treatment.
3. The method according to Claim 1 or 2, characterized in that the separated water is returned into the method for reuse.
4. The method according to Claim 1, characterized in that the waste stream from the pickling baths to be recycled is separated in a suitable separating system into a first partial stream having the metal salts to be recycled and a second partial stream having free acids, which is conducted back into the pickling bath.

5. The method according to Claim 4, characterized in that the residues of free acids existing in the first partial stream are converted into metal salts according to step a) using metal hydroxides, oxides, or carbonates of the metals used in the pickling bath.
6. The method according to Claim 5, characterized in that the treated first partial stream having metal salts is converted in a system for separating water after step b) into a concentrated metal salt solution near the solubility limit of the metal salts.
7. The method according to Claim 6, characterized in that the water separated in step b) is returned to the separating system as process water in the form of a slightly acidic distillate.
8. The method according to one of Claims 4 through 7, characterized in that the first partial stream is mixed before step a) with the acid waste stream from the rinsing baths/air washers.
9. The method according to Claim 6, characterized in that the concentrated metal salt solution from the pickling baths and possibly the rinsing baths and air washers is supplied to a thermal method for decomposing the salts into metal oxides and free acids according to step c).

10. The method according to Claim 1, characterized in that the rinsing water and/or the waste water of the rinsing baths/air washers are neutralized using a chemical, particularly sodium hydroxide solution or potassium hydroxide solution, through which the acid residues are left in dissolved form, but the metals are precipitated.
11. The method according to Claim 10, characterized in that the precipitated and filtered metal salts are supplied to step a), particularly as metal hydroxides, for converting the free acid into metal salts.
12. The method according to Claim 10, characterized in that the neutralized waste water is converted in a system for separating water into a concentrated salt solution near the solubility limit of the metal salt and the distillate generated is used again for rinsing purposes.
13. The method according to Claim 12, characterized in that the concentrated salt solution is converted in a system for salt decomposition, particularly a cationic exchanger or electrodialysis system, into acids and bases for reuse in the process.
14. The method according to at least one of the preceding claims, characterized in that a steel pickling bath is used as the metal pickling bath.
15. The method according to Claim 14, characterized in that a stainless steel pickling bath is used as the steel pickling bath.

16. A device for recycling metal pickling baths (1), including the associated rinsing baths/air washers (4), which has:
- at least one system (5) for converting the free acids present in the liquid waste streams (2, 6) to be treated into the metal salt form before recycling,
 - at least one system for separating water (12, 27) from the metal salt solution obtained, which is as free of acids as possible, in order to obtain a concentrated metal salt solution, and
 - at least one system for thermal salt decomposition (3) of the salt concentrate streams from the pickling baths (1) and the washers/air washers (4) to obtain metal oxides and free acids.
17. The device according to Claim 16, characterized by a separating system (13) for separating the waste stream to be recycled from the pickling baths (1) into a first partial stream (19) having the metal salts to be recycled and a second partial stream (18) having free acids, which is returned into the pickling bath (1).
18. The device according to Claim 17, characterized in that the separating system (13) represents an acid regeneration system, particularly an acid retardation or diffusion dialysis system.

19. The device according to one of Claims 16 through 18, characterized in that the system for thermal salt decomposition represents a roaster (3).
20. The device according to one of Claims 16 through 19, characterized by lines to a concentrator (12, 27), particularly an evaporator, for the first partial stream (19) and/or the accumulated rinsing and exhaust air water (22, 26, 6a).
21. The device according to Claim 20, characterized in that a reactor (5) is provided before the concentrator (12), in which the free acids present may be converted into metal salts by adding a reagent (11).
22. The device according to Claim 21, characterized in that the reagent (11) represents a metal hydroxide of the metal which is also present in the pickling bath.
23. The device according to at least one of the preceding claims, characterized in that a system (24) is provided in which the metals from the waste stream (6) of the rinsing baths/air washers (4) may be precipitated and filtered off by adding a neutralization chemical, and the reagent (11) obtained may be supplied to the reactor (5).
24. The device according to at least one of Claims 16 through 23, characterized in that the supply volume to the system for thermal salt decomposition (3) is set via the concentrator (12), in order to keep the volume stream (15) to the system (3) small.

25. The device according to at least one of Claims 16 through 24, characterized in that a system for water separation (29), particularly an electrolysis system, is provided for the metal salt solution concentrated from rinsing and exhaust air water (26) in the concentrator (27).